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(54) POLYESTER RESIN FOR TONER, ITS PRODUCTION AND TONER USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a polyester resin useful as a dry toner by making the polyester resin comprising a terephthalic acid component, etc., a polyfunctional carboxylic acid, etc., an aliphatic diol component and another diol component contain antimony, etc., and a phosphorus atom in satisfying with a specific condition.

SOLUTION: This polyester resin is obtained by comprising 70-100 mol.% based on the whole acid component of terephthalic acid component and/or isophthalic acid component, 0.1-30 mol.% base on the whole acid component of a polyfunctional carboxylic acid having more than three function and/or a polyhydric alcohol component having more than three hydric value, 40-120 mol.% based on the whole acid component of an aliphatic diol component and 0-80 mol.%, based on the whole acid component of another diol component, and containing 10-100 ppm of at least one kind of metal atom selected from the group of antimony, titanium, tin, zinc and manganese and 3-30 ppm of phosphorus atom, in satisfying with the formula: $2.0 \leq (M/P) \leq 5.0$ {M is weight of the metal atom (ppm); P is weight of the phosphorus atom (ppm)}, and has 100-150°C softening point, ≤ 5 mgKOH/g acid value and 1,000-10,000 number-average molecular weight.

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CLAIMS

[Claim(s)]

[Claim 1] As opposed to all acid components 70-100-mol % a terephthalic-acid component and/or an isophthalic acid component at least (a) A kind, (b) As opposed to all acid components the multiple-valued carboxylic acid more than 0.1 - 30-mol trivalent [% of] and/or the polyhydric-alcohol component more than trivalent at least A kind, (c) It is polyester resin which consists of a diol component of 0 - 80-mol % of others to 40 - 120-mol % an aliphatic series diol component and the all (d) acid components to all acid components. 10-100 ppm and the Lynn atom for a kind of metal [at least] atom chosen from the group which consists of antimony, titanium, tin, zinc, and manganese into this polyester resin in 2-30 ppm And polyester resin for toners with which it contains so that the following formula (I) may be satisfied, and softening temperature is characterized by 100-150 degrees C and the acid number being [5 or less mgKOH/g and number average molecular weight] 1,000-10,000.

[Equation 1] $2.0 \leq M/P \leq 5.0$ (I)

(M expresses the weight (ppm) of a metal atom among a formula, and P expresses the weight (ppm) of the Lynn atom.)

[Claim 2] As opposed to all acid components 70-100-mol % a terephthalic-acid component and/or an isophthalic acid component at least (a) A kind, (b) As opposed to all acid components the multiple-valued carboxylic acid more than 0.1 - 30-mol trivalent [% of] and/or the polyhydric-alcohol component more than trivalent at least A kind, (c) 40 - 120-mol % an aliphatic series diol component and the all (d) acid components are received to all acid components. The diol component of 0 - 80-mol % of others It mixes so that the mole ratio of an alcoholic component to an acid component may become 2.0 or less. Under the existence of at least a kind of the metallic compounds containing antimony, titanium, tin, zinc, and manganese After performing an esterification reaction or an ester conversion reaction at the temperature of 140 degrees C or more, Phosphorus compounds are added, when an aliphatic series diol component is made to distill out of a system under the pressure of 500 or less mmHg, a polycondensation is performed and the melt viscosity of a reaction mixture goes up. 10-100 ppm and the Lynn atom for a kind of metal [at least] atom chosen from the group which consists of antimony, titanium, tin, zinc, and manganese into the resin obtained in 2-30 ppm And the manufacture approach of the polyester resin for toners according to claim 1 that it contains so that the following type (I) may be satisfied, and softening temperature is characterized by 100-150 degrees C and the acid number manufacturing the polyester resin 5 or less mgKOH/g and whose number average molecular weight are 1,000-10,000.

[Equation 2] $2.0 \leq M/P \leq 5.0$ (I)

(M expresses the weight (ppm) of a metal atom among a formula, and P expresses the weight (ppm) of the Lynn atom.)

[Claim 3] The toner containing polyester resin and a coloring agent according to claim 1.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to polyester resin useful as a dry type toner used for the development of an electrostatic-charge image or a magnetic latent image, and its manufacture approach in a xerography, an electrostatic recording method, an electrostatic printing method, etc. It excels in blocking resistance, a melting fluidity, low-temperature fixable one, and an electrification property in more detail. It is related with the high-speed copying machine with which the object for full color as which a high melting fluidity is required especially, and low-temperature fixable one are demanded and the polyester resin for toners useful as an object for high speed printers, its manufacture approach, and the toner using it.

[0002]

[Description of the Prior Art] In the approach of obtaining **** more lasting than an electrostatic-charge image, it is established, after developing negatives with the toner which electrified beforehand the electrostatic-charge image formed on the photoconductivity photo conductor or the electrostatic recording object by friction. In the case of a magnetic latent image, it is established after developing the latent image on a magnetic drum with the toner containing the magnetic substance. Fixing is performed by carrying out welding of this on an imprint sheet, after carrying out welding of the toner image obtained by development on the photoconductivity photo conductor or the electrostatic recording object directly or imprinting a toner image on paper or a film. Although welding of a toner image is performed by contact with a solvent steam, pressurization, and heating and there are a non-contacted heating method in electric oven and a sticking-by-pressure heating method with a pressurization roller as heating method, recently when improvement in the speed of a fixing process is demanded, the latter is mainly used.

[0003] There are 1 component system toner and a two-component system toner as toner used by the dry-developing method. After carrying out melting kneading and, fully distributing resin, a coloring agent, an electric charge control agent, and a required additive in addition to this first, coarse grinding of the two-component system toner is carried out, and subsequently it is pulverized, classifies in a predetermined size range and is manufactured. 1 component system toner adds the magnetic iron powder other than each component of the toner of the above-mentioned two-component system, and is manufactured similarly.

[0004] Since resin is a principal component under toner combination, it governs most engine performance required of a toner. For this reason, in toner manufacture, it is required for the resin for toners that the dispersibility of the coloring agent in a melting kneading process and the grindability in a grinding process should be good etc., and busy engine performance -- fixable, un-offsetting nature, blocking resistance, and an electrical property are good -- is required of it in use of a toner. As resin used for manufacture of a toner, although an epoxy resin, polyester resin, polystyrene resin, methacrylic system resin, etc. are well-known, as for

the object for sticking-by-pressure heating fixing methods, the copolymer of styrene and acrylic ester (meta) has mainly been used.

[0005] Furthermore, in order to obtain a color picture, the toner of three to 4 color must be made to have to adhere to a transfer paper, and subsequently in a fixing process, you have to color, carrying out various melting mixing, and have to make it established in an above-mentioned development process. the binder for full color toners -- resin with the sufficient miscibility in a fixing process like **** -- if it puts in another way, good resin of a melting fluidity is desired strongly. When the good binder of a melting fluidity is used, there is a problem which the offset phenomenon in a fixing process produces. However, if a binder is made to take the structure of cross linkage or is made to giant-molecule-ize, in order to prevent an offset phenomenon, since a melting fluidity will fall, as binder resin for full color toners, it is not suitable. Therefore, silicone oil etc. is applied to a fixing roller front face in order to obtain un-offsetting nature in the case of the copying machine for full color. There are not few examples for which the technique of offset prevention, such as applying a silicone oil etc. to a fixing roller, is used also in the common copying machine except full color and the printer recently when improvement in the speed of the fixing section and energy saving are desired strongly.

[0006] In the binder resin used for the object for full color toners, or the toner for high-speed copying machines, it is necessary to hypoviscosity-ize for melting mixing or low energy melting. For this reason, in the case of polyester resin, it is desirable as a combination of the acid component suitable for hypoviscosity-ization, and an alcoholic component to use aromatic series dicarboxylic acid and aliphatic series diol. However, in order to give elasticity to polyester resin, when the multifunctional compound more than trivalent was used as a polymerization component, since reactivity was high, it was difficult [it] to obtain the polyester resin which has suitable viscosity easily therefore as for stopping the viscosity rise under polymerization reaction.

[0007]

[Problem(s) to be Solved by the Invention] As for the place which this invention is made in order to cancel the above faults, and is made into the purpose, a melting fluidity and low-temperature fixable one are good, and are to offer the polyester resin for toners excellent in blocking resistance, and its manufacture approach.

[0008]

[Means for Solving the Problem] As a result of advancing examination wholeheartedly that said purpose should be attained, this invention persons found out that the polyester resin which has the specific physical properties acquired by the specific manufacture approach including the multiple-valued carboxylic acid and/or polyhydric alcohol more than trivalent as a polymer component could attain the purpose, and completed this invention while they used the specific component of the amount of specification for the acid component and the diol component.

[0009] This invention receives the all (a) acid components. 70 - 100-mol % a terephthalic-acid component and/or an isophthalic acid component at least Namely, a kind, (b) As opposed to all acid components the multiple-valued carboxylic acid more than 0.1 - 30-mol trivalent [% of] and/or the polyhydric-alcohol component more than trivalent at least A kind, (c) It is polyester resin which consists of a diol component of 0 - 80-mol % of others to 40 - 120-mol % an aliphatic series diol component and the all (d) acid components to all acid components. 10-100 ppm and the Lynn atom for a kind of metal [at least] atom chosen from the group which consists of antimony, titanium, tin, zinc, and manganese into this polyester resin in 2-30 ppm And it contains so that the following type (I) may be satisfied, and 100-150 degrees C and the acid number have softening temperature in the polyester resin for toners with which 5 or less mgKOH/g and number average molecular weight are characterized by being 1,000-10,000.

[Equation 3] $2.0 \leq M/P \leq 5.0$ (I)

(M expresses the weight (ppm) of a metal atom among a formula, and P expresses the weight

(ppm) of the Lynn atom.)

[0010] This invention receives the all (a) acid components. 70 - 100-mol % a terephthalic-acid component and/or an isophthalic acid component at least Moreover, a kind, (b) As opposed to all acid components the multiple-valued carboxylic acid more than 0.1 - 30-mol trivalent [% of] and/or the polyhydric-alcohol component more than trivalent at least A kind, (c) 40 - 120-mol % an aliphatic series diol component and the all (d) acid components are received to all acid components. The diol component of 0 - 80-mol % of others It mixes so that the mole ratio of an alcoholic component to an acid component may become 2.0 or less. Under the existence of at least a kind of the metallic compounds containing antimony, titanium, tin, zinc, and manganese After performing an esterification reaction or an ester conversion reaction at the temperature of 140 degrees C or more, Phosphorus compounds are added, when an aliphatic series diol component is made to distill out of a system under the pressure of 500 or less mmHg, a polycondensation is performed and the melt viscosity of a reaction mixture goes up. 10-100 ppm and the Lynn atom for a kind of metal [at least] atom chosen from the group which consists of antimony, titanium, tin, zinc, and manganese into the resin obtained in 2-30 ppm And it contains so that the following type (I) may be satisfied, and softening temperature is in the manufacture approach of the above-mentioned polyester resin for toners that 100-150 degrees C and the acid number are characterized by 5 or less mgKOH/g and number average molecular weight manufacturing the polyester resin which is 1,000-10,000.

[Equation 4] $2.0 \leq M/P \leq 5.0$ (I)

(M expresses the weight (ppm) of a metal atom among a formula, and P expresses the weight (ppm) of the Lynn atom.)

[0011] Moreover, this invention is in the toner containing above-mentioned polyester resin and an above-mentioned coloring agent.

[0012]

[Embodiment of the Invention] the polyester resin of this invention -- (a) terephthalic-acid component and/or a terephthalic-acid component -- at least -- the multiple-valued carboxylic-acid component more than a kind and (b) trivalent, and/or the polyhydric-alcohol component more than trivalent -- it consists of a kind, a (c) aliphatic series diol component, and a diol component besides (d) at least.

[0013] It is used for constituting the (a) component in this invention. A terephthalic acid and/or isophthalic acid consist of a terephthalic acid, isophthalic acid, and those low-grade alkyl ester. As an example of the low-grade alkyl ester of a terephthalic acid and isophthalic acid, although there are dimethyl terephthalate, isophthalic acid dimethyl, terephthalic-acid diethyl, isophthalic acid diethyl, terephthalic-acid dibutyl, isophthalic acid dibutyl, etc., for example, dimethyl terephthalate and isophthalic acid dimethyl are desirable in respect of cost and handling. These dicarboxylic acid or the low-grade alkyl ester of those is a kind, or it is used for it for two or more sorts, using together. since the above-mentioned dicarboxylic acid is effective in raising the glass transition temperature (it being hereafter written as Tg.) of the resin obtained, and raising the blocking resistance of a toner -- all acid components -- receiving -- 70-100-mol % -- it is used 80-100-mol% of preferably.

[0014] Moreover, as an example of the other dicarboxylic acid which can be used in this invention, these acid anhydrides, such as a phthalic acid, a sebacic acid, an isodecyl succinic acid, a dodecenyl succinic acid, a maleic acid, a fumaric acid, adipic acids and these monomethyl, monoethyl, dimethyl, and diethyl ester, are mentioned. Since these 2 base carboxylic acids affect fixable and blocking resistance of a toner greatly, it is desirable to use it in the range which does not check the purpose of this invention according to the military requirement.

[0015] The multiple-valued carboxylic acid more than trivalent [which is used for constituting the (b) component in this invention] and/or the polyhydric alcohol more than trivalent are

chosen from the multiple-valued carboxylic acid more than trivalent, and the polyhydric alcohol more than trivalent. As an example of the multiple-valued carboxylic acid more than trivalent, trimellitic acid, pyromellitic acid, 1 and 2, 4-cyclohexane tricarboxylic acid, 2 and 5, 7-naphthalene tricarboxylic acid, 1 and 2, 4-naphthalene tricarboxylic acid, 1 and 2, 5-hexane tricarboxylic acid, 1, 2 and 7, 8-octane tetracarboxylic acid, these acid anhydrides, etc. can be mentioned. moreover -- as the polyhydric alcohol more than trivalent -- for example, sorbitol, 1, 2 and 3, 6-hexa tetra-rol, 1, 4-sorbitan, pentaerythritol, dipentaerythritol, tripentaerythritol, 1 and 2, 4-butane triol, 1 and 2, 5-PENTA triol, glycerol, and 2-methyl - 1, 2, 3-propane triol, and 2-methyl - 1, 2, 4-butane triol, trimethylol propane, 1 and 3, 5-trihydroxy methylbenzene, etc. are mentioned. Also in these, especially use of trimellitic acid and its acid anhydride, pentaerythritol, and trimethylol propane is desirable. the multiple-valued carboxylic acid more than trivalent [these], and the polyhydric alcohol more than trivalent -- a kind -- or two or more sorts are used together and it is used. these components -- copolymerized polyester resin -- bridge formation or the effectiveness which is made to branching-ize and raises un-offsetting nature -- it is -- the content -- all acid components -- receiving -- 0.1-30-mol % -- it is 0.1-27-mol % preferably. The toner using the polyester resin with which, as for this, the amount used exceeds 30-mol % has low number average molecular weight, and is because it is in the inclination which is inferior in fixable.

[0016] As aliphatic series diol used for constituting the (c) component in this invention Ethylene glycol, 1, 2-propanediol, 1,3-propanediol, 1, 2-butanediol, 1,3-butanediol, 1,4-butanediol, Neopentyl glycol, 2-ethyl-isobutane -1, 3-diol, The 2-butyl-2-ethyl propane -1, 3-diol, 1,6-hexanediol, 1, 4-cyclohexane dimethanol, hydrogenation bisphenol A, etc. are mentioned, and they are used for a kind or two sorts or more by these, using together. Ethylene glycol, neopentyl glycol, 1, and 4-cyclohexane dimethanol is desirable from the fixable point of a toner also in these. (c) since a component is effective in lowering the melt viscosity of polyester resin -- the content -- all dicarboxylic acid components -- receiving -- 40-120-mol % -- it is 60-110-mol % preferably.

[0017] As an example of the diol of others which are used for constituting the (d) component in this invention Polyoxyethylene - (2.0) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (2.0) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene -(2.2)-Polyoxyethylene - (2.0) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (6.0) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (2.2) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (2.3) -2, 2-screw (4-hydroxyphenyl) propane,